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Four hundred and ninety-third meeting.

March 12, 1861. — MONTHLY MEETING.

The PRESIDENT in the chair.

Professor Horsford exhibited excellent drawings, by Mr. Hand, of New York, of magnified dissections and preparations of the grain of wheat, especially of the coats and superficial portion or *bran*, which has been long since ascertained to contain the principal part of the gluten, this indicating the importance of retaining as much of the bran in the bread as possible.

Professor C. W. Eliot read the following paper: —

On the Chromate of Chromium, and analogous Chromates, with a New View of the Constitution of the Black Oxide of Manganese. By FRANK H. STORER and CHARLES W. ELIOT.

I. CHROMATE OF CHROMIUM (Cr_2O_3 CrO_3).

1. When a solution of monochromate of potash is mixed with a solution of any ter-salt of chromic oxide, the mixture immediately becomes brownish red, a bright brown precipitate subsides, and when this precipitate has been completely deposited, the liquid separated by filtration will present the clear yellowish-red color of bichromate of potash. The chrome salt may be chrome alum, or sulphate of chromic oxide, or hydrated sesquichloride of chromium, and, if a sufficient excess of chromate of potash be added to the solution, the precipitate and the filtrate will present the appearances described. This filtrate may be evaporated and crystallized; the resulting crystals will be a mixture of bichromate of potash and of sulphate of potash or chloride of potassium, as the case may be: often crystals of monochromate of potash will also present themselves. We prepared the precipitate for analysis by mixing a solution of chrome alum with an excess of monochromate of potash. The brown precipitate was washed with cold water: the color of the wash-water, at first bright yellow, became gradually paler, but never colorless. Twice in the course of the seven days during which the washing was continued, the precipitate was transferred from the filter to a mortar, stirred up with water, and thrown upon a fresh filter. This pro-

cess deepened the yellow color of the wash-water in each case. It being quite evident that the color of the wash-water was due to chromic acid abstracted from the precipitate, the washing was stopped on the eighth day, the precipitate was dried at 50° to 55°, and analyzed as follows. A portion was dissolved in very dilute nitric acid by the aid of a gentle heat; the color of the solution was a red brown. Ammonia, added in very slight excess to this solution, kept at the boiling point for half an hour, produced a brownish-green precipitate of chromic oxide, which looked the browner because it floated in a bright yellow liquid. This precipitate was filtered off and thoroughly washed with hot water; it then presented the common appearance of chromic oxide, and was ignited and weighed in the usual manner. The filtrate from this precipitate and the wash-waters were concentrated by evaporation, and acidified with acetic acid. Acetate of lead then precipitated the whole of the chromic acid contained in the yellow liquid, and after the subsidence of the precipitate the supernatant liquid was perfectly colorless. The chromate of lead was washed and weighed on a tared filter as usual. The result of the analysis was

CrO_3 = 16.27 per cent
Cr_2O_3 = 46.43 " "
Water = 37.30 " " (by difference).

This examination showed, first, that the washed precipitate was a compound of chromic acid and chromic oxide; secondly, that it was more basic than any supposable definite compound of these two bodies; thirdly, that the prolonged washing removed chromic acid from the substance originally precipitated. To study the effect of the washing upon the precipitate, we prepared a considerable quantity of the brown precipitate by mixing a concentrated solution of pure chrome alum with a large excess of a concentrated solution of monochromate of potash. The precipitate as first collected upon the filter of course retained a considerable quantity of the bichromate of potash, chromate of potash, and sulphate of potash which existed in the filtrate. The precipitate was quickly rinsed with cold water until these mechanically adhering salts seemed to have been removed. During this short washing the substance underwent no change in color or in any other external property. A portion was now removed from the filter, air-dried on a brick, and submitted to analysis (analysis *a*). The rest of the precipitate was washed for six hours with cold water; another portion was then taken from the filter, air-dried, and analyzed (analysis *b*). Through the remainder (perhaps two teaspoonfuls) of the precipitate five litres of water were passed; another portion was then dried at 100° and analyzed (analysis *c*). When dried at 100° the precipitate is much less readily soluble in dilute nitric acid, than when not so heated, but the difficulty is easily overcome. The method of analysis was that described above.

Analyses.

	a.	*b.*	*c.*
Cr_2O_3	39.69 per cent.	45.26 per cent.	65.17 per cent.
CrO_3	22.42 " "	15.12 " "	8.87 " "
HO (by diff.)	37.89 " "	39.62 " "	25.96 " "

A comparison of these three determinations teaches that the abstraction of chromic acid by washing with cold water stops at no definite point, and probably has no limit except the complete change of the original precipitate into chromic oxide. The composition of the substance *a* must be a close approximation to the composition of the original precipitate, for the slight rinsing which was intended merely to remove the chromates belonging to the filtrate could hardly have abstracted much of its combined chromic acid. In the chromate of chromium whose formula would be Cr_2O_3 CrO_3, the ratio of the chromic oxide to the chromic acid would be that of 3 : 2; and we find that the ratio of the chromic oxide to the chromic acid in analysis *a* is but little larger than that of 3 : 2. The substance *a* is probably therefore a chromate of chromium of the formula Cr_2O_3 CrO_3, from which a little of the chromic acid has been removed by washing.

Assuming for the present that the precipitate produced by the reaction of chrome alum on monochromate of potash is in truth this chromate of chromium, let us inquire into the nature of the reaction between these two salts by which this precipitate could be formed, and bichromate of potash left in the filtrate. Concentrated solutions of pure chrome alum and of pure monochromate of potash were prepared of known strengths, in order to determine the amount of either solution required to produce a precipitate in the other. A single drop of chrome alum solution produces an immediate and permanent precipitate in the chromate solution; but if the process be reversed and the solution of monochromate of potash be dropped into the alum solution, no permanent precipitate is formed till an apparently large excess of chromate of potash has been added. By accurate quantitative experiments we have proved that five equivalents of chromate of potash must be added to one equivalent of chrome alum to effect precipitation. If a less quantity be added, any precipitate which may form will at once redissolve when the mixture is made complete by agitation.* The reaction between the two salts may therefore be expressed by the formula,

$$5\,(KO\,CrO_3) + KO\,SO_3,\ Cr_2O_3\ 3\,SO_3 = 4\,(KO\,SO_3) + 2\,(KO\,2\,CrO_3) + Cr_3O_3\,CrO_3\,,$$

and if to one equivalent of chrome alum more than five equivalents of chromate of potash be added, the excess above five remains inactive.

$$x\,(KO\,CrO_3) + KO\,SO_3,\ Cr_2O_3\ 3\,SO_3 = 4\,(KO\,SO_3) + 2\,(KO\,2\,CrO_3) + Cr_2O_3\,CrO_3 + (x - 5)\ (KO\,CrO_3).$$

If any other normal salt of chromic oxide be used, a similar formula will express the reaction; thus: —

$$Cr_2Cl_3 + 5\ (KO\ CrO_3) = 3\ (K\ Cl) + 2\ (KO\ 2\ CrO_3) + Cr_2O_3\ CrO_3.$$

$$Cr_2O_3\ 3\ SO_3 + 5\ (KO\ CrO_3) = 3\ (KO\ SO_3) + 2\ (KO\ 2\ CrO_3) + Cr_2O_3\ CrO_3.$$

With the exact proportions of chrome alum and chromate of potash which are by the formula necessary for the precipitation of chromate of chromium we prepared a quantity of the precipitate for a second series of analyses in corroboration of analyses *a*, *b*, and *c*. The precipitate thrown upon a filter was very slightly rinsed with cold water, a portion of it was taken off, pressed between folds of filter-paper under heavy weights, and air-dried for analysis (analysis *d*); the rest of the precipitate was washed for six hours till no trace of the filtrate could possibly be supposed to be retained by the precipitate, when another portion was taken out for analysis, pressed, and air-dried (analysis *e*); lastly five litres of water were passed through the remaining precipitate, which was then dried at 100° and submitted to analysis (analysis *f*). The process of analysis was the same described above, and the results were as follows: —

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* In this connection we would call attention to the inaccuracy of the statement made by Berzelius in his *Traité de Chimie,* (Paris, 1846, Vol. II. 307), to the effect that a compound whose formula is $Cr_2O_3\ 3\ CrO_3$ is precipitated, when a few drops of the solution of monochromate of potash are added to the solution of a neutral chrome salt. No permanent precipitate whatever is produced under these circumstances, as any one may satisfy himself by repeating the simple experiment described above.

Analyses.

	d.	*e.*	*f.*
Cr_2O_3	38.85 per cent.	44.01 per cent.	59.83 per cent.
CrO_3	25.91 " "	19.88 " "	13.43 " "
HO (by diff.)	35.24 " "	36.11 " "	26.74 " "

This set of analyses corroborates the first series in every respect, and the ratio of the chromic oxide to the chromic acid of the substance *d* is almost precisely the ratio 3 : 2 of the chromic oxide to the chromic acid in the chromate of chromium Cr_2O_3 CrO_3. We again see that there is no definite limit to the removal of chromic acid by prolonged washing, and that the substance may be readily made more basic than any imaginable definite compound of chromic oxide and chromic acid would be.

In these analyses the precipitates had been somewhat washed before any analysis was made; it remained to analyze the substance precipitated with so much of the adhering filtrate as could not be removed by pressure between folds of filter-paper without washing. One precipitate (analysis *g*) was prepared by mixing a solution of one equivalent of chrome alum with eight equivalents of chromate of potash in solution, and a second by mixing a solution of one equivalent of chrome alum with sixteen equivalents of chromate of potash in solution (analysis *h*). In both cases the solutions used were concentrated and the precipitates air-dried. The method of analysis which we had heretofore employed was open to one objection, — a trace of chromic oxide was liable to be dissolved in the excess of ammonia, to be again separated when the filtrate and wash-waters from the chromic oxide precipitate were concentrated by evaporation, and the process would obviously be altogether inadmissible in any case where the sulphates of the mother-liquor had not been removed by washing before submitting the precipitate to analysis, since sulphate of lead would be formed and vitiate the determination of the chromic acid. We therefore resorted to Rose's method of separating chromic oxide from chromic acid, by means of the nitrate of the suboxide of mercury.* The solution of the substance to be analyzed in dilute nitric acid was nearly neutralized with carbonate of potash, and when the carbonic acid had been allowed sufficient time to escape, nitrate of the suboxide of mercury was added, the precipitate filtered off, washed, strongly ignited, and the chromic acid calculated from the pure chromic oxide which remained. To the filtrate from this first precipitate ammonia in excess was added, and the washed precipitate, strongly ignited, was the chromic oxide contained in the original substance.

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* Handbuch der Analytischen Chemie, (Braunschweig, 1851,) II. 379.

Analyses.

	g.	*h.*
Cr_2O_3	33.06 per cent.	33.54 per cent.
CrO_3	32.03 " "	30.53 " "
HO (by difference)	34.91 " "	35.93 " "

It is quite evident from these analyses that the precipitate caused by mixing chromate of potash with a neutral chrome salt cannot contain more than one equivalent of chromic acid in combination with its chromic oxide, since in the above determinations the chromic acid is nearer one equivalent than two with reference to the chromic oxide found, in spite of the fact that the considerable amount of chromic acid which, combined with potash, has adhered mechanically to the precipitate, is thrown down by the nitrate of the suboxide of mercury, together with the chromic acid which was originally united to the chromic oxide. But the fact that the substance under examination cannot be purified by washing without altering its constitution, renders it impossible to ascertain the exact composition of the body by the methods of analysis heretofore used, or by any similar methods; for this purpose the process used by Vogel * in analyzing this same substance, obtained by him from a different source and miscalled CrO_2, is admirably adapted. The precipitate examined by this method was not washed at all, but was simply dried by pressure between folds of filter-paper and exposure to the air. A weighed portion was placed in the bulb of a reduction-tube, with which a weighed chloride of calcium tube was connected; a current of dry air was then drawn through the apparatus, and the reduction-tube was cautiously heated till all the water of the precipitate had been absorbed by the weighed chloride of calcium tube, the heat finally rising to dull redness. The salts with which the precipitate under examination was contaminated were sulphate of potash, bichromate of potash, and a little chromate of potash, and since the solutions from which the precipitate was prepared were concentrated, it was to be expected that a considerable quantity of these salts would adhere to the precipitate; but since all these salts are fixed at a low red heat, they were not altered by the heat to which the precipitate was exposed. The rest of the precipitate must have lost by the ignition all its water and all the oxygen over and above that necessary to the constitution of chromic oxide. By subtracting the weight of the water collected from the total loss by ignition, the weight of the oxygen expelled is obtained. The ignited residue was then washed out of the bulb of the reduction-tube, digested in hot water, thrown upon a filter and washed with hot water till only pure chromic oxide remained; lastly, this oxide was ignited and weighed. By subtracting the weight of the chromic oxide from the weight of the whole ignited residue, the weight of the soluble salts which adhered mechanically to the precipitate was obtained. The following are the figures of an analysis by this method: —

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* Jour. pr. Ch., LXXVII. 484 (1859).

Weight of reduction-tube + precipitate	10.3848	gram.
“ “ “	9.6136	“
“ “ precipitate	0.7712	“
Weight of reduction-tube after ignition	10.2673	“
Loss by ignition	0.1175	“
Weight of residue	0.6537	“
Weight of CaCl tube after ignition	17.4196	“
“ “ “ “ before “	17.3204	“
“ “ water	0.0992	“
“ “ oxygen = .1175 — .0992 =	0.0183	“
Weight of crucible + Cr_2O_3	13.1275	“
“ “ “ + filter ash	12.9601	“
“ “ Cr_2O_3	0.1674	“
“ “ soluble salts = .6537 — .1674 =	0.4863	“

In the compound whose formula is Cr_2O_3 CrO_3, the ratio of the number of atoms of oxygen to the number of atoms of chromium is that of 2 : 1. By adding another equivalent of oxygen to the chromic oxide found, we shall make the ratio of the atoms of oxygen to the atoms of chromium that of the compound Cr_2O_3 CrO_3. Hence the proportion.

(Equiv. Cr_2O_3)		(Equiv. O) =	(Cr_2O_3 found)		(1 equiv. O)
76.48	:	8	= 0.1674	:	$x = 0.0175$

If the original precipitate was the compound whose formula is Cr_2O_3 CrO_3, the loss of oxygen by ignition would have been 0.0175 gram.; the actual loss was 0.0183 gram., being within 0.0008 gram. of the theoretical amount. A loss of eight tenths of a milligramme in the water determination would of course account for this very small excess of oxygen.

A second analysis by this method of a precipitate containing a smaller proportion of soluble salts corroborated the first determination in every respect, and left no doubt that the true composition of the precipitate produced in the aqueous solution of a neutral salt of chromic oxide by the solution of chromate of potash is represented by the formula Cr_2O_3 CrO_3.

2. Schweitzer* observed that, when nitric oxide is passed through a moderately dilute solution of bichromate of potash, a brown precipitate separates after some time, especially if the liquid be slightly warmed. He did not analyze the substance, but remarks that it presents all the appearance of the brown oxide of chromium (so called). We prepared this compound by passing a stream of nitric oxide through a very dilute solution of bichromate of potash (a strong solution will not give the reaction so readily, if, indeed, at all) for three hours; in a few minutes the liquid became dark-colored and ceased to be transparent, but after standing twenty-four hours, during four of which it had been gently heated, there was still no apparent deposit; it was again warmed, and after sixteen hours more a slimy red-brown deposit was found at the bottom of the vessel. During forty-eight hours longer this deposit was allowed to accumulate, when the supernatant liquid was decanted and the precipitate thrown upon a filter. The decanted fluid continued to deposit very slowly this red-brown matter for days and weeks; indeed, in this, and several similar experiments, we have found no limit of time to the continuous, though very gradual, accumulation of this deposit. The slimy precipitate which had been filtered off was washed with hot water for twelve hours, the water at first coming through of a dark-red color, but growing gradually paler till it retained only a feeble yellow. The washing was continued for a week with cold water, and more than nine litres of water passed through the small precipitate. Whenever the color of the wash-water became so

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* Jour. Pr. Ch., XXXIX. 269 (1846).

pale as to be hardly perceptible except with a considerable thickness of liquid, it was only necessary to transfer the precipitate to a mortar, rub it with water and throw it upon a fresh filter, in order greatly to intensify the yellow color of the filtrate. Believing that the chromic acid which colored the wash-water was derived from the decomposition of the precipitate, we stopped the washing on the eighth day, dried the precipitate at 50° – 55°, and analyzed it by the first method described above. The color of the solution of the substance in dilute nitric acid was red-brown, and of the precipitate produced by ammonia, dirty green, which washing changed to the usual color of chromic oxide. The result of the analysis was, —

Cr_2O_3 = 53.31 per cent.
CrO_3 = 18.64 " "
HO (by difference) = 28.05 " "

In regard to the ratio of the chromic oxide to the chromic acid, this result is very much like that of the first analysis given above (page 193), and leads to the same conclusions, viz. that the original precipitate is a compound of chromic oxide and chromic acid, from which prolonged washing abstracts chromic acid to an indefinite extent. We next prepared a new precipitate by passing nitric oxide through a dilute solution of bichromate of potash, and, without washing it at all, pressed it between folds of filter-paper, dried it by exposure to the air, and analyzed it by Rose's method, above described, with the following result: —

Cr_2O_3 = 28.55 per cent.
CrO_3 = 29.33 " "
HO (by difference) = 42.12 " "

The object of this analysis was to prove that, even when the precipitate was contaminated with the chromates of the filtrate, the proportion of the chromic acid to the chromic oxide fell far below that which would exist in a compound containing two equivalents of chromic acid to one of chromic oxide, thus making it probable that the true formula of the precipitate is $Cr_2O_3\ CrO_3$.

To determine the exact proportions of chromic oxide and chromic acid in the original substance evidently requires a different process of analysis, and the third method of analysis described above is applicable to this purpose, with this advantage over the case to which we first applied it, that the precipitate separates from such a dilute solution as to carry but a small proportion of soluble salts into the wholly unwashed deposit. The following are the figures of such an analysis of the precipitate pressed between folds of filter-paper without washing, and air-dried.

Weight of the reduction-tube + precipitate	9.1856	gram.
“ “ “	8.5520	“
“ “ precipitate	0.6336	“
“ “ reduction-tube after ignition	8.9342	“
Loss by ignition	0.2514	“
Weight of residue	0.3822	“
Weight of CaCl tube after ignition	17.6352	“
“ “ “ before “	17.4210	“
“ “ water	0.2142	“
“ “ oxygen = .2514 — .2142	.0372	“
Weight of crucible + Cr_2O_3	35.0227	“
“ “ “ + filter ash	34.7345	“
“ “ Cr_2O_3	.2882	“
“ “ soluble salts = .3822 — .2882 =	.0940	“

(Equiv. Cr_2O_3) : (Equiv. O) = (Cr_2O_3 found) : (1 equiv. O).

The proportion 76.48 : 8 = .2882 : x = .0302 gives the theoretical amount of oxygen necessary to bring the chromic oxide found up to the composition expressed by the formula Cr_2O_3 CrO_3 at 0.0302 gram.; the oxygen actually found was 0.0372 gram., being seven milligrammes in excess of the theoretical amount. When it is remembered that the unavoidable loss in the water determination, however small, tends to increase the amount of oxygen found, and that the loss in the chromic oxide determination tends to decrease the theoretical amount of oxygen, a discrepancy of only seven milligrammes will be considered allowable. A second analysis of the same precipitate by the same method gave even a nearer result, viz.: —

Oxygen required to raise the Cr_2O_3 found to the composition Cr_2O_3 CrO_3	0.0235	gram.
Oxygen actually found	0.0264	“

These two analyses, in connection with the preceding determinations by the other methods, seem to us to prove conclusively that the precipitate produced by passing nitric oxide through a solution of bichromate of potash is a chromate of chromic oxide, having the formula Cr_2O_3 CrO_3. Schweitzer expressed his conception of the reaction by the formula

$$4\,(KO\;2\;CrO_3) + 2\;NO_2 = 2\,(KO\;CrO_3) + 2\,(KO\;NO_5) + 6\,(CrO_2);$$

we shall write it, in accordance with the results of our analyses,

$$2\,(KO\;2\;CrO_3) + NO_2 = KO\;NO_5 + KO\;CrO_3 + Cr_2O_3\;CrO_3.$$

3. The same partial reduction of the chromic acid in bichromate of potash, which in the reaction just described is effected by nitric oxide, may be accomplished by alcohol with the aid of light. The precipitate so produced has been analyzed by Vogel,* who assigns to it the composition which would be expressed by the formula Cr_2O_3 CrO_3, though, for reasons hereafter to be considered, he seems to prefer the formula CrO_2. The precipitate thus obtained by alcohol† is identical in color and texture with that produced by nitric oxide, or by the double reaction between a neutral salt of chromic oxide and monochromate of potash. It is unnecessary in this connection to refer to the well-known reduction of aqueous chromic acid by sulphurous acid, by certain organic acids, by alcohol, and by paper; light and heat facilitate the reduction, and the brown chromate of chromic oxide is often produced when the reduction is but partial.‡

4. Again, the chromate of chromic oxide may be obtained by the oxidation of the hydrate of chromic oxide. When pure hydrated chromic oxide is treated with chlorine water, the oxide is converted into the brown chromate of chromic oxide, provided that the quantity of chlorine water be not sufficient to effect the solution of the chromate of chromic oxide formed in the chlorhydric acid which results from the reaction. Of course, the chromate of chromic oxide cannot be pre-

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* Jour. pr. Ch., LXXVII. 482, (1859,) and Dingler's Polyt. J., CLIII. 391.

† We desire to correct a serious misprint in Vogel's note, as given in the Journal für praktische Chemie (LXXVII. 482), and thence transferred into Kopp & Will's Jahresbericht für 1859, p. 171. In the second line of the Article, "Ammoniak" should be "Alkohol." We trust this correction may save others the trouble we took before it occurred to us that the error was a typographical one, in endeavoring to verify or account for the marvellous statement that bichromate of potash was reduced by ammonia. The word is correctly printed in the abridgment of the same article given in Dingler's Journal, CLIII. 391.

‡ Gmelin's Handbook (Cavendish Soc. Ed.), IV. 119.

pared for analysis in this way, because a mixture of substances is the result to be expected from the incomplete reaction. Again, the partial oxidation of hydrated chromic oxide may be effected by exposing it for a long time to a temperature above 200°, but below redness, with free access of air.*

The most precise statement on this subject has been made by Krüger,† whose main purpose was to prove that the glowing of ignited chromic oxide was due to the sudden escape of oxygen absorbed at a lower temperature, but who incidentally maintains that this absorption of oxygen gives rise to a definite oxide of chromium whose formula is CrO_2. We think to be able to show, first, that no definite compound whatever is formed during this imperfect oxidation; secondly, that the substance which really results from the prolonged heating contains chromic acid, and is an indeterminate approximation to the body whose formula is Cr_2O_3 CrO_3. It is obviously impossible to expose all parts of a substance in powder, like the hydrated chromic oxide, to the uniform action of the same quantity of air at the same temperature for the same time, and the limits of temperature between which the desired absorption of oxygen will take place most readily are not very clearly defined. Under these circumstances we should expect to obtain, not a definite compound, but a mixture, and the figures of Krüger's own analysis fully confirm this expectation. Krüger found 63.70 per cent of chromium and 36.30 per cent of oxygen in the body which he analyzed; the supposed oxide of chromium, CrO_2, would contain 62.12 per cent of chromium, giving a discrepancy of 1.58 per cent between the chromium of Krüger's substance and the chromium of the imaginary CrO_2. This does not seem an inadmissible error, till we observe that the whole difference between the chromium in chromic oxide (68.62 per cent) with which Krüger began, and the chromium in the supposed higher oxide CrO_2 (62.12 per cent), is only 6.50 per cent, and that his error of 1.58 per cent in the amount of chromium is therefore nearly twenty-five per cent of the whole difference between the bodies Cr_2O_3 and CrO_2. With so fatal a discrepancy between the actual and the theoretical figures, it is of course impossible to maintain that a definite oxide is obtained by such an indefinite process. We pass to the second point, the existence of chromic acid in imperfectly oxidized chromic oxide. Krüger thought to disprove the presence of chromic acid by heating the substance with sulphuric acid and common salt; no chromate of chloride of chromium being visible, he inferred the absence of chromic acid. This test is at best but an unsatisfactory one when applied to a very insoluble substance containing only a small proportion of chromic acid, and there seems to be no reason for trusting to a coarse reaction in a difficult case when very delicate tests are at hand. By heating hydrated chromic oxide for five hours to a temperature varying between 200° and 210° we obtained a brownish black powder, which dissolved with great difficulty in dilute acids, communicating a dark yellow color to the liquid. Digested with water, the powder yielded a partial solution of a bright yellow color, and this solution gave a very marked reaction for perchromic acid with the solution of peroxide of hydrogen.* When quickly boiled with an aqueous solution of chloride of ammonium, the filtered solution was bright yellow, and gave the reaction of perchromic acid with peroxide of hydrogen. Would it not be difficult to explain this effect of aqueous chloride of ammonium on the brown powder on the supposition that its real composition was represented by the formula CrO_2? Krüger endeavored to strengthen his position with regard to the absence of chromic acid, by heating with common salt and sulphuric acid a precipitate prepared by mixing bichromate of potash, sulphate of chromic oxide, and ammonia, and finding as before no chromate of chloride of chromium; he used the precipitate in one experiment air-dried, in another, dried at 110°. This precipitate was probably a mixture of chromic oxide with the chromate of chromic oxide, and, unless the last ingredient was present in very small proportion, it should have readily produced chromate of chloride of chromium. From a portion of the precipitate used in analysis *f*, we obtained without difficulty the red chromate of chloride of chromium by heating it with chloride of sodium and strong sulphuric acid. We shall have occasion to cite below a similar experiment upon an anhydrous mixture of chromic oxide and chromic acid, obtained by gently igniting the nitrate of chromic oxide, in which the chromate of the chloride of chromium was very readily obtained. Relying on the yellow color imparted by the substance under examination to water and to chloride of ammonium, and on the ready exhibition of perchromic acid by means of peroxide of hydrogen, and explaining Krüger's failure to obtain chlorochromic acid by the fact that only a very small amount of chromic acid proportionally exists in the mixture, we conclude that, by long heating in the air, a part of the chromic oxide is converted into chromic acid, which instantly combines with other chromic oxide, and that the end of this process, seldom if ever attained, is the conversion of the whole mass into the chromate of chromic oxide, $Cr_2O_3\ CrO_3$.

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* The partial conversion of chromic oxide into chromic acid by gentle roasting seems to have been applied in the arts years ago. Cooley, in his Cyclopædia of Practical Receipts, (London, 1845, p. 263,) describes Charles Watt's process of preparing chromic acid from the oxide of chromium precipitated by lime from the residual liquor of the process of bleaching with chromic acid. The precipitate was heated evenly in a thin layer on a flat iron plate, with frequent stirring, till the mass assumed a yellow color. If too much heat was employed, the product of this operation was easily decomposed, assuming a green color. This process was apparently a true conversion of chromic oxide into chromic acid by roasting, and should not be confounded with the method of preparing chromate of lime described by Jacquelain (Ann. de Ch. et de Phys., [3.] XXI. 478), in which a mixture of lime and chrome-iron ore was heated to redness in a reverberatory furnace.

† Jour. pr. Ch., XXXII. 383, (1844,) and Pogg. Ann., LXI. pp. 219, 406.

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* Storer, Proc. Amer. Acad., IV. 138; Jour. pr. Ch., LXXX. 44.

5. Many chemists, among whom may be mentioned Vauquelin, Berzelius, Döbereiner, and Thomson, have tried the experiment of gently igniting the nitrate of chromic oxide, or, what amounts to the same thing, of evaporating to dryness nitric acid in contact with metallic chromium or hydrated chromic oxide, and moderately heating the residue. Some, like Berzelius,* have thought that they obtained in this way a definite oxide of chromium, intermediate between chromic oxide and chromic acid, and answering to the formula CrO_2; others, like Vauquelin,† have imagined that they obtained chromic acid by repeated evaporation of nitric acid with chromium, or have believed, with Thomson ‡ and Godon,§ that a great part of the green oxide was converted into chromic acid; while others still have maintained, with Döbereiner, ‖ that the chromate of chromic oxide was formed by the decomposition of the nitrate.

In order to a clear knowledge of the effect of evaporating nitric acid with chromic oxide, it is necessary in the first place to answer qualitatively the question, Is chromic acid formed during the process? A mixture of nitric acid and hydrated chromic oxide was gently evaporated, first on a water-bath, then upon a sand-bath, and before the free nitric acid was completely driven off, a portion of the moist mass was treated with a solution of caustic potash; it partially dissolved with a yellow color, and the solution gave the distinct blue of perchromic acid with peroxide of hydrogen. The rest of the evaporated residue was heated till it looked like a perfectly dry powder, but still retained the smell of nitric acid. In this condition a portion was treated with water, in which it slowly and partially dissolved, yielding a brownish yellow solution, which readily gave the blue of perchromic acid. A half of the remaining residue from the original evaporation was strongly heated in a porcelain dish on a sand-bath, and then digested with water during four hours; the solution so obtained was decidedly yellow, and gave easily the blue of perchromic acid. The other half of the residue was heated on platinum foil, till the platinum was of a dull red color in a darkened room, and was then soaked in water for thirty-six hours; the supernatant liquid was of a pale yellow color, and gave a faint blue with peroxide of hydrogen. The same substance treated with caustic potash gave a yellow solution.

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* Thomson's Ann. Phil., III. 104, (1814,) and Schweigger's J. für Ch. u. Phys., XXII. 56.

† Ann. de Chim., XXV. 201 (1798).

‡ Phil. Trans., 1827, Part I. p. 206.

§ Rapport par MM. Berthollet et Vauquelin, Ann. de Ch., LIII. 224.

‖ Schweigger's Jour. für Ch. u. Phys., XXII. 482 (1818).

With this qualitative evidence of the formation of an abundance of chromic acid at a moderate temperature, which is not wholly destroyed even at incipient redness, we proceeded to the quantitative determination of the amount of chromic acid formed at the different stages of the process. A quantity of pure hydrated chromic oxide was treated in a porcelain dish with an excess of pure nitric acid, and evaporated on a water-bath nearly to dryness; those parts of the substance which dried completely were moistened with nitric acid and again dried. The nitric acid could not be completely driven off on the water-bath; though the larger part of the mass seemed dry, yet portions of it were still moist when the process was stopped, and it was far from being homogeneous. The brownish black substance imparted a strong yellow tinge to water, and dissolved with difficulty in dilute nitric acid, giving a brownish yellow solution. A portion of it, analyzed by Rose's method, gave

Cr_2O_3 = 64.85 per cent.
CrO_3 = 31.51 "
NO_5 and HO = 3.64 " (by difference).

It was now necessary to prepare for analysis from the evaporated residue a series of homogeneous substances, each of which had been exposed to a little higher temperature than the preceding one, in order to exhibit the effect of different temperatures in the production of chromic acid. A portion (No. 1) of the evaporated residue was heated on a porcelain dish at a low temperature, with constant stirring, to complete dryness; a second portion (No. 2) was first thoroughly dried at the same temperature to which No. 1 had been exposed, and was then somewhat more strongly, but still very gently, heated for a few moments, during which nitrous fumes escaped in abundance; in this manner each substance was dried at the highest temperature to which the preceding one had been exposed, and was then subjected to a little stronger heat during five or ten minutes; the last substance (No. 5) was heated as hot as was possible, while avoiding incipient redness. The chromic acid of each substance was determined by precipitating it with nitrate of the suboxide of mercury; the chromic oxide was also determined in two or three cases, but only to control the analyses. All five substances were soaked in water for five hours; pure nitric acid was then added in very small quantity, and, at the end of forty-four hours more, solution had been effected in each case. The color of the dry powder was brownish black, that of the solutions brownish yellow. The percentage of chromic acid in each substance was as follows: —

	CrO_3.
No. 1,	25.18 per cent.
No. 2,	26.09 "
No. 3,	48.52 "
No. 4,	55.49 "
No. 5,	60.39 "

It therefore appears that a variable amount of chromic oxide may be converted into chromic acid by evaporation with nitric acid, and that the quantity so changed increases with the increase of temperature till incipient redness is reached. If this mixture of chromic oxide, chromic acid, and nitric acid be exposed to a red heat, the nitric acid and the absorbed oxygen are driven off together, and nothing remains but insoluble chromic oxide. It is sufficiently clear from these results, that no definite compound can be formed during this evaporation of nitric acid in contact with chromic oxide; the result is simply an indeterminate mixture of chromic oxide and chromic acid. It may be remarked, in passing, that this mixture closely resembles in every external property the brownish black powder obtained by gently heating chromic oxide in contact with the air, a substance which, as we have seen, is also an indeterminate mixture of chromic oxide and chromic acid, containing, however, very much less chromic acid than the mixture just examined. Substance No. 5 of the preceding series, although anhydrous, yields chlorochromic acid with salt and sulphuric acid with the greatest facility, another indication that the true explanation of Krüger's not obtaining chlorochromic acid from his heated chromic oxide is to be found in the fact that it contains too small an amount of chromic acid to be exhibited by that somewhat coarse reaction.

6. Many distinguished chemists have observed the reactions and studied several of the substances which we have here described, and no treatment of the subject can be complete which does not embrace an abstract of their labors. We shall therefore relate as concisely as possible the history of the substance which has been variously called brown oxide of chromium, or chromate of chromic oxide, and review the discussion as to its composition which has heretofore been brought to no satisfactory conclusion.

Vauquelin,* the discoverer of chromium, obtained what he thought to be a brownish-red oxide of chromium by several methods, the details of which it is unnecessary to describe; it will be enough to observe, that neither of his methods gave him a definite compound; they all gave rise to indeterminate mixtures of the bodies now known as chromic oxide and chromic acid. He proved that nitric acid, whether cold or boiling, cannot oxidize chromic oxide, but that the calcination of the nitrate of chromic oxide produced a substance whose aqueous solution was red; ammonia precipitated from this solution the green oxide, and the separated filtrate was yellow. His experiments led Vauquelin to the conclusion, that there are two kinds of oxide of chromium, which differ only in the quantity of oxygen they contain.

Two errors, into which the reader of Vauquelin's papers might easily fall, demand notice. It might be inferred from some of his statements that the chromate of ammonia was a body readily decomposed by simple boiling with separation of the so-called brown oxide of chromium. We have found the chromate of ammonia to be a body possessing much greater stability than has been usually attributed to it; its aqueous solution will resist, without change, prolonged boiling, concentration, and exposure for weeks to the direct rays of the sun. It is true that repeated evaporation to dryness may partially decompose it, and it is of course destroyed by ignition.

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* Ann. de Ch., LXX. pp. 85, 86 (1809).

Again, Vauquelin asserts that ammonia will precipitate the brown oxide of chromium from an aqueous solution of chromic acid through which sulphurous acid has been passed, and this assertion seems to be confirmed by some statements, made without quoted authority in Gmelin's Handbook (Cavendish Soc. Ed., IV. 114), concerning salts of the brown oxide of chromium obtained by dissolving this hydrated oxide in acids, from which solutions it may be again precipitated by ammonia. This is an important point in determining the real existence of such an oxide of chromium, and we have therefore made it the subject of careful experiment. We have dissolved in dilute chlorhydric and dilute nitric acids such precipitates as analysis had shown to have very nearly the composition which is expressed by the formula CrO_2 (as, for instance, the precipitate of analysis *d*, and of the analysis on page 201), and have added to the solutions ammonia of every strength, from the strongest to the weakest, and have so obtained one invariable result, viz. a precipitate of common green chromic oxide, and a filtrate made yellow by chromate of ammonia. It is true that the fresh precipitate has a dirty or brownish look, caused by its impregnation with the yellow liquid in which it floats; and this is the most probable explanation of the opinion held by some previous observers, that this precipitate was something more than ordinary chromic oxide.

The chief authority upon which the existence of salts of the brown oxide of chromium is asserted, seems to be that of Brandenburg,* who obtained solutions of substances which his own experiments, rightly interpreted, prove to have been mixtures of chromic acid and salts of chromic oxide, but which he thought were salts of an imaginary higher oxide of chromium. There is no such thing as a salt of the brown oxide of chromium, for the reason that there is no such base.

It was the opinion of Döbereiner† that the substance produced by the calcination of the nitrate of chromic oxide was a chromate of chromic oxide and not an oxide of chromium, and he referred to the same formula the substances formed by the reduction of chromic acid by paper, and by the digestion of chromic oxide with chromic acid.

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* Schweigger, Jour. für Ch. u. Phys., XIII. 287 - 289 and 299 - 304.

† Ibid., XXII. 482 (1818).

Thomson[*] prepared a brown precipitate, which he called brown oxide of chromium, by passing a stream of sulphurous acid through a solution of chromate or bichromate of potash. We have found, as did Berthier,[†] that no precipitate whatever is produced by passing sulphurous acid through bichromate of potash; but this is a point of no importance in this connection. Thomson washed the precipitate which he had obtained for two months, and noticed the steady abstraction of chromic acid from the precipitate. He finally analyzed the washed oxide (as he called it) and made it to be a very basic chromate corresponding to the formula $(Cr_2O_3)_6 CrO_3$. His opinion of the effect produced by the ignition of the nitrate of chromic oxide we have already cited. Under the head of chromate of chromium he remarks that, when chromic oxide is dissolved in chromic acid and the solution evaporated, there remains a substance quite similar in appearance to the brown oxide of chromium. Again, he observed the precipitate produced by mixing chromate of potash with sesquichloride of chromium, and says of it that it is evidently composed of chromic acid and the green oxide of chromium. Guided by the analogy of chromium and iron, he prepared a chromate of iron by mixing chromate of potash with sesquichloride of iron; an analysis of the edulcorated brown precipitate led him to the formula $(Fe_2O_3)_5 CrO_3$, and in the filtrate and wash-water he thought he found another less basic chromate, corresponding to the formula $(Fe_2O_3)_5 (CrO_3)_{2.5}$. On the whole, Thomson seems to have believed in the existence of a brown oxide of chromium, intermediate between chromic oxide and chromic acid; but every one of his experiments and analyses points directly to the conclusion, that the supposed oxide is in reality a chromate of chromic oxide, or rather in most cases an indeterminate mixture of chromic oxide and chromic acid.

We come now to the researches of Maus,[‡] contemporaneous with those of Thomson, but much more conclusive upon the disputed point as to the existence of a distinct oxide of chromium answering to the formula CrO_2. Maus mixed an aqueous solution of sesquichloride of chromium with chromate of potash, and digested the washed precipitate with acetate of lead, thereby obtaining a green solution of acetate of chromic oxide and a yellow precipitate of chromate of lead; he treated the same substance with arsenic acid, and obtained the insoluble arseniate of chromic oxide and chromic acid in solution. By washing the original precipitate for three weeks he claims to have removed all the chromic acid, and says that nothing but chromic oxide remained. By mixing sesquichloride of iron with chromate of potash he prepared a similar chromate of iron, from which all the chromic acid could be removed by washing in the same way. He believed that the calcination of the nitrate of chromic oxide produced a chromate of chromium, but containing always nitric acid, because a heat sufficient to drive off all the nitric acid also converted the chromate of chromium into chromic oxide. Maus did not analyze quantitatively any of these precipitates, probably because he was embarrassed by the impurities from which he could not free the precipitates without altering their composition; but his qualitative results are amply sufficient to prove that they all contained chromic acid as part of their original constitution. Maus did analyze two substances prepared by digesting chromic oxide and ferric oxide in chromic acid; the results of these analyses were, —

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[*] Phil. Trans., 1827, Part I. p. 186.

[†] Ann. der Ch. u. Pharm., XLVI. 185 (1843).

[‡] Pogg. Ann., IX. 127 (1827).

1.	2.
$Cr_2O_3 = 27.79$ per cent.	$Fe_2O_3 = 25.06$ per cent.
$CrO_3 = 72.21$ "	$CrO_3 = 74.94$ "

And he assigned to them the formulæ $Cr_2O_3\ 2\ CrO_3$ and $Fe_2O_3\ 2\ CrO_3$ respectively. These formulæ are incorrect; the figures of the first analysis would give about four equivalents of acid to one of the oxide, and those of the second analysis would give more than four equivalents of chromic acid to one of ferric oxide. Both substances were unquestionably indeterminate mixtures. Dumas, recounting the experiments of Maus, says, "These results would be decisive, but they are contested by Berzelius." * It is therefore necessary to review the opinions of Berzelius on this subject.

In 1814 Berzelius, writing an essay on the "Cause of Chemical Proportions," † mentions the new oxide of chromium, prepared by Vauquelin, intermediate between the green oxide and chromic acid. Berzelius

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* Traité de Chimie Appliq., (Liége, 1848,) VII. 319.

† Thomson's Ann. Phil., III. 104, (1814,) and Schweigger's Jour. für Ch. u. Phys., XXII. 56.

prepared this oxide, as he supposed, by igniting the nitrate of chromic oxide, observed the external properties of the substance, but did not analyze it, and made use of it only as an aid in establishing the contents of oxygen in chromic acid. In this essay he states the formulæ of the oxides of chromium as CrO_3, CrO_4, and CrO_6, the last being the acid. In a subsequent paper,* in speaking of the oxides of chromium, he lays special stress upon the close relation between manganese and chromium, and on the isomorphism of the sesquioxides of aluminum, chromium, manganese, and iron. He now writes the formula of chromic oxide as Cr_2O_3, and in all probability the peroxide of manganese (MnO_2) was in his mind an argument for the oxide CrO_2, though he does not mention it in the paper referred to. Finally, in 1829, Berzelius† rejects the conclusions arrived at by Maus, and gives the following reasons for his continued belief in the existence of the oxide CrO_2. The first reason urged is the analogy between the sulphur acids and the oxides of chromium; this comparison is based merely on the isomorphism of chromic and sulphuric acids. In the light of the better knowledge both of the sulphur acids and of the oxides of chromium which thirty years have given us, and with the clearer notions of chemical classification which now prevail, we can find in the existence of sulphurous acid no argument for the existence of an oxide of chromium containing two atoms of oxygen. Secondly, Berzelius gives his own idea of the reaction consequent upon mixing chromate of potash with sesquichloride of chromium, which he thinks is not correctly described by Maus; according to Berzelius, the decomposition between these two salts does not take place at once, but the mixed solution first becomes dark yellow, soon changes to brown, a brown precipitate separates, and the liquid remains brown; hence he infers the formation of two compounds of chromium and oxygen, one soluble and represented by the formula Cr_2O_5, the other the insoluble CrO_2. We have accurately described in the first sentences of this paper the phenomena presented on mixing a solution of sesquichloride of chromium with a solution of chromate of potash, and have subsequently given the formula which represents the reaction. There is no reason to suppose that any such compound as Cr_2O_5 remains in solution; when the brown precipitate first formed has completely subsided, the color of the filtrate is that of bichromate of potash. Lastly, Berzelius accounts for the fact that the supposed oxide yields to analysis chromic acid and chromic oxide by imagining that the original oxide is decomposed by contact with water into chromic acid and chromic oxide, as hyposulphurous acid is decomposed by water into sulphurous acid and sulphur, or as nitrous acid is resolved by water above 0° into nitric oxide and a solution of nitric acid ($3\,NO_3 + Aq = 2\,NO_2 + NO_5 + Aq$). This might perhaps be a possible supposition, if the brown substance in question were prepared by methods in which water had no part; but when we see it precipitated from dilute solutions of monochromate of potash and a neutral chrome salt, or subsiding in the course of days from a very dilute solution of bichromate of potash, we are forced to the conclusion, that the substance is from the first composed of the chromic acid and chromic oxide which analysis shows it to contain. In short, we have all the evidence, analytical and synthetical, that this brown precipitate is a chromate of chromic oxide, which we have of the real constitution of sulphate of potash.

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* Pogg. Ann., VII. 415 (1826).

† In his Jahresbericht, VIII. 123.

The compound is well worthy the attention of those chemists who deny that formulæ ever express the actual constitution of bodies; it seems questionable whether any formula for the chromate of chromium can readily be written on the unitary theory which will express its properties and reactions as well as the dualistic formula. When at this distance we look back at the feebleness of the theoretical arguments which Berzelius opposed to the facts of Maus, Thomson, Döbereiner, and others, we marvel at the weight of a name whose authority outweighed the accumulated evidence of several trustworthy observers, and prevented the truth from prevailing thirty-four years ago. Berzelius himself became much less confident in after years of the truth of his earlier views; in his *Traité de Chimie*[*] he calls the precipitate formed by mixing a neutral chrome salt with chromate of potash, chromate of chromic oxide, and in a subsequent paragraph merely says that it is very possible that this compound is the oxide of chromium, CrO_2.

An observation made by Rammelsberg[†] added something to our knowledge of the precipitate formed by mixing a solution of chrome alum with a solution of chromate of potash. He made a determination of the water contained in the washed precipitate, and weighed the chromic oxide obtained by igniting it; the oxygen which was expelled by ignition was determined by loss. The analysis led to the formula $(Cr_2O_3)_3\,(CrO_3)_2 + 9\,HO$, showing that the washing of the precipitate had been sufficient to make it somewhat basic. The point specially noticeable in Rammelsberg's statement is his assertion that the precipitate was washed till it imparted no color to cold water. This is not credible, for the testimony of all other chemists is unanimous upon the point, that there is no limit to the removal of chromic acid by washing from this precipitate. We have often prepared much more basic precipitates, and have never yet seen colorless wash-water from the most basic of them. The color may become so pale as not to be very noticeable in small vessels.

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[*] II. 307 (Paris, 1846).

[†] Pogg. Ann., LXVIII. 274 (1846).

The discussion which we have traced left the subject in such doubt and obscurity, that most writers of text-books have given both views of the substance in question, some leaning to one theory of its composition, some to the other. In our endeavor to settle the question, we shall next bring to bear upon the subject the arguments to be drawn from analogy.

II. Analogous Chromates.

The metals with which chromium is allied are aluminum, iron, and manganese, and the existence of chromates of the sesquioxides of these metals with properties analogous to those which we have described as belonging to the chromate of chromic oxide, will be additional evidence that this substance is rightly so called.

1. *Chromate of Alumina.* Maus* observed, but did not analyze, the chromate of alumina which is precipitated when chromate of potash is added to a solution of alumina in chromic acid; he speaks of it as "consisting of chromic acid with much alumina." When the precipitate was thoroughly washed, pure hydrate of alumina remained on the filter and acid chromate of alumina passed into the filtrate. Fairrie† also describes a chromate of alumina prepared by mixing alum solution with the solution of chromate of potash, and his analysis led to the exact formula $Al_2O_3\ CrO_3$; he states, however, that the precipitate was thoroughly washed, which in connection with the result of his analysis is quite incomprehensible; for Maus observed, and our own experiments fully confirm his observation, that all the chromic acid may be readily washed out of this compound.

The yellow precipitate which appears when chromate of potash is dropped into a solution of alum, is constantly re-dissolved until the proportion of chromate of potash added amounts to five equivalents to each one of alum; the precipitate then becomes permanent; it is light yellow in color, and has a gelatinous appearance which suggests an excess of alumina. The reaction is evidently the same as that above given for the precipitation of chromate of chromic oxide. $5\,(KO\ CrO_3) + Al_2O_3\ 3\,SO_3,\ KO\ SO_3 = 4\,(KO\ SO_3) + 2\,(KO\ 2\,CrO_3) + Al_2O_3\ CrO_3$. The precipitate was drained, pressed between folds of filter-paper under heavy weights, and air-dried. The filtrate, when evaporated and crystallized, gave crystals of bichromate of potash, and of sulphate of potash mixed with the slight excess of chromate of potash. The presence of soluble salts in the pressed precipitate, and its decomposition by washing, determined us to the third method of analysis above described (p. 197). Omitting the subsidiary weighings, we give the essential figures of our first analysis of this substance.

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* Pogg. Ann., XI. 82 (1827).

† Jour. Chem. Soc., IV. 301 (1852).

Weight of the precipitate analyzed	0.5997	gram.
" " water found	0.1948	"
" " oxygen "	0.0197	"
" " soluble salts found	0.1969	"
" " mixed precipitate of $Cr_2O_3 + Al_2O_3$	0.1883	"

It will be remembered that the water and the precipitate of chromic oxide and alumina are actually weighed, the oxygen being determined by subtracting the water found from the total loss by ignition, and the soluble salts by subtracting the weight of the precipitate of chromic oxide and alumina from the weight of the whole residue after ignition. The amount of chromate of alumina corresponding to the oxygen lost by ignition may be calculated as follows: — ignition drives off half of the oxygen originally combined with the chromium; hence

Oxygen in the chromic acid of precipitate = 0.0394
Chromic acid corresponding to this oxygen = 0.0825
Chromate of alumina " " chromic acid = 0.1666

This calculation rests entirely upon the single determination of the oxygen, and an inspection of the steps of the process will show that any error in the amount of oxygen, or rather in the water determination on which the weight of oxygen depends, is multiplied by eight and a fraction in the calculated amount of chromate of alumina. A considerable discrepancy is therefore to be expected between the amount of chromate of alumina so calculated, and the amount actually found in the analysis, the sum of the oxygen and of the mixed precipitate of chromic oxide and alumina. That sum is in this analysis 0.208 gram.; subtracting the calculated amount 0.1666 gram., we find a discrepancy of 0.0414 gram. By subtracting 0.005 gram. only from the weight of the water determined, this error would be corrected, and the precipitate would coincide exactly with the formula $Al_2O_3\ CrO_3$, or, as the figures stand, its composition is very nearly that represented by the formula $(Al_2O_3)_3\ (CrO_3)_2$. Of course a method of analysis involving such a multiplication of an error, however small, is objectionable, but we were at a loss to devise a better. A second analysis gave a similar result; the discrepancy between the calculated and the actual numbers was four milligrammes larger than in the first analysis, and the figures of the analysis gave a chromate of alumina a little more basic than that represented by the formula $(Al_2O_3)_3\ (CrO_3)_2$. We attach very little importance to any such formula. The fact seems to be that the normal composition of the chromate of alumina precipitated by the double decomposition of alum and chromate of potash is represented by the formula $Al_2O_3\ CrO_3$, but that the compound is a feeble one, and parts readily with some of its chromic acid to the water of the solutions from which it is precipitated; hence the basic character of the precipitate analyzed. How Fairrie obtained a thoroughly washed chromate of alumina having the formula $Al_2O_3\ CrO_3$ is a mystery upon which our experiments have thrown no light.

2. *Chromate of Iron.* We have already cited the observations of Thomson concerning this chromate, which he found after washing to be very basic, and also the statement of Maus concerning the acid chromate of iron with four equivalents of chromic acid, obtained by digesting hydrated sesquioxide of iron in aqueous chromic acid. It remained for us to analyze, as exactly as the circumstances permit, the unwashed chromate of iron which is precipitated when chromate of potash is mixed with perchloride of iron. The method of analysis was the same as that used for chromate of alumina, with the disadvantage that the error in the amount of oxygen found is multiplied by ten instead of by eight in calculating the chromate of iron, because the atomic weight of the sesquioxide of iron is larger than that of alumina. The stability of the chromate of iron is greater, however, than that of the chromate of alumina, and the results of the analyses are very much nearer to the formula $Fe_2O_3\ CrO_3$, than those of chromate of alumina to the formula $Al_2O_3\ CrO_3$. The formula for the reaction whereby the brown chro-

mate of iron is precipitated, is the same as those already given for chromate of chromic oxide and chromate of alumina, viz.: —

$$Fe_2Cl_3 + 5\ (KO\ CrO_3) = 3\ (KCl) + 2\ (KO\ 2\ CrO_3) + Fe_2O_3\ CrO_3.$$

Until the requisite amount of chromate of potash had been added to the perchloride of iron, the precipitate re-dissolved; when it became permanent, it was drained, pressed, and air-dried for analysis.

Analysis 1.

Weight of the precipitate analyzed,	0.6626	gram.
" " water found,	0.0966	"
" " oxygen "	0.0395	"
" " soluble salts found,	0.2288	"
" " mixed precipitate of $Fe_2O_3 + Cr_2O_3$,	0.2977	"

From these data may be obtained by the necessary proportions, —

Oxygen in the chromic acid of precipitate,	0.0790
Chromic acid corresponding to this oxygen,	0.1654
Chromate of iron corresponding to this chromic acid,	0.4287

Chromate of iron found = $Fe_2O_3 + Cr_2O_3 + O$ weighed = 0.3943
Excess of the calculated chromate of iron over the found = 0.0344

This error would be perfectly corrected by a loss of three milligrammes in the water determination, or as the figures stand without any correction they would lead to the conclusion that the precipitate was a chromate of iron of the formula $Fe_2O_3\ CrO_3$, but containing a very small excess of chromic acid.

Analysis 2.

Weight of the precipitate analyzed,	0.6590
" " water found,	0.0990
" " oxygen "	0.0360
" " soluble salts found,	0.2254
" " mixed precipitate of $Fe_2O_3 + Cr_2O_3$,	0.2986

From these data may be obtained by the necessary proportions, —

Oxygen in the chromic acid of precipitate,	0.0720
Chromic acid corresponding to this oxygen,	0.1197
Chromate of iron corresponding to this chromic acid,	0.3597

Chromate of iron found = $Fe_2O_3 + Cr_2O_3 + O$ weighed = 0.3346
Excess of the calculated chromate of iron over the found = 0.0251

This error would be corrected by a supposed loss of little more than two milligrammes in the water determination. This second analysis, therefore, confirms the view that the normal composition of this chromate of iron is represented by the formula $Fe_2O_3\ CrO_3$.

It is unnecessary to call attention to the great similarity of the properties of the chromates of chromic oxide, ferric oxide, and alumina; their normal composition is represented by the formula $R_2O_3\ CrO_3$, but they are such feeble compounds as seldom to be found of the exact constitution which the formula indicates.* Of the three, the chromate of chromic oxide is the most stable, and we have been able to prepare it with the exact theoretical composition, from which it so easily varies. It should be observed, that a variation in the composition of these chromates, amounting to even ten per cent of their chromic acid, does not affect in the least their external properties, and it is by no means impossible that they are examples of that variation in the law of definite proportions which has been ably discussed by Professor J. P. Cooke in the Memoirs of this Academy; † but unfortunately, as must often be the case, the limits of error of our methods of analysis are wider than those of the supposed variation, and moreover, on this border-land between the kingdoms of Chemical and of Mechanical Force, there must always be doubt and difference of opinion concerning the cause to which a proved effect is to be ascribed.

3. *Chromate of Manganese.* The existence of this chromate has been so clearly demonstrated by previous observers that we have thought it unnecessary to add any experiments of our own. On mixing a solution of sulphate of the protoxide of manganese with a solution of chromate of potash, a chocolate-colored precipitate subsides after some time, to which Warington ‡ assigned the formula $(MnO)_2\ CrO_3\ 2\ HO$. Bensch § also analyzed a similar precipitate, for which he gives the same formula. In Warington's analysis the amount of protoxide of manganese is larger than the compound which his formula rep-

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* The monochromate of glucina mentioned by Gmelin (Handbook, IV. 155, Cavendish Soc. Ed.) evidently belongs to this class.

† New Series, V. pp. 348, 352 (1854).

‡ Phil. Mag., [3.] XXI. 380 (1842).

§ Pogg. Ann., LV. 98 (1842).

resents would contain, and it is, moreover, questionable if the protoxide of manganese could exist in contact with chromic acid. The subsequent observations of Fairrie * explain these difficulties. He mixed the solutions of chloride of manganese and chromate of potash, and so obtained a precipitate whose composition by analysis was $3\,(Mn_2O_3\ CrO_3) + Cr_2O_3 + 6\,HO$. Fairrie's criticism on the analyses of Warington and Bensch, that they overlooked the chromic oxide formed by the reaction, is no doubt just. He also remarks, that the precipitate appeared to be formed by the action of seven equivalents of chromate of potash on six equivalents of chloride of manganese, but offers no explanation of the reaction. The decomposition is explained by the formula,

$$7\,(KO\ CrO_3) + 6\,(MnCl) = 3\ Mn_2O_3\ CrO_3) + Cr_2O_3 + 6\,(K\,Cl) + KO\ 2\ CrO_3.$$

Six equivalents of the protoxide of manganese are oxidized into three equivalents of sesquioxide of manganese, at the expense of the three atoms of oxygen which two equivalents of chromic acid give up in changing into one equivalent of chromic oxide; probably the chromic oxide so formed enters into combination with the chromate of manganese, rendering it basic. Chloride of potassium and bichromate of potash remain in the filtrate.†

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* Jour. Chem. Soc., IV. 300 (1852).

† We do not wish to leave the subject of the metallic chromates without noticing the remarkable analyses published by Malaguti and Sarzeau (Ann. de Ch. et de Phys., [3.] IX. 431, 1843) of the chromates of copper, zinc, cadmium, and nickel. The figures of these analyses correspond exactly with the following singular formulæ : —

$(CuO)_4\ CrO_3 + 5\ HO$, $(CdO)_5\ (CrO_3)_2 + 8\ HO$,
$(ZnO)_4\ CrO_3 + 5\ HO$, $(NiO)_4\ CrO_3 + 6\ HO$.

All these precipitates were washed with boiling water till no color came from them, and it is clear that these chromates, like those which we have studied, may be deprived of the greater part of their chromic acid, if not the whole, by prolonged washing; hence the basic character of the substances analyzed. The marvel is, that the analyses corresponded so exactly with such peculiar formulæ ; it is hardly conceivable that the publication of many analyses of each of these substances should not show the existence of a series of compounds, which conform to no definite formulæ.

III. The Black Oxide of Manganese ($3\ MnO_2 = Mn_2O_3\ MnO_3$).

Another question now suggests itself, — Would analogy lead us to suppose that there was an oxide of chromium containing two atoms of oxygen? Comparing chromium, as before, with the allied metals, aluminum, iron, and manganese, we meet with no such oxide of aluminum, and we have Fremy's * direct statement that he could find no oxide of the formula FeO_2. Manganese, however, forms a compound with oxygen, stable, insoluble, and natural, which has heretofore always been spoken of as an oxide of manganese and been represented by the formula MnO_2. Is not the existence of this compound a strong argument for the oxide CrO_2? We propose to adduce the evidence which makes it most probable that this so-called peroxide of manganese is in reality a compound, sometimes definite but oftener indefinite, of manganic acid and manganic oxide, and that its normal composition is to be represented by the formula $Mn_2O_3\ MnO_3$.

We shall not expect to resolve this substance into manganic oxide and manganic acid with the same facility with which we analyze the chromate of chromic oxide. This latter body is less stable than either chromic oxide or chromic acid, whereas manganic acid and oxide are both exceedingly unstable substances, obtained with difficulty but easily destroyed. On the other hand, there is no more stable compound of manganese than that called the peroxide. It is not therefore decomposed, as the chromate of chromium is, by boiling water, boiling caustic potash, or a boiling solution of chloride of ammonium. We prepared artificial peroxide of manganese by passing a stream of chlorine through water in which carbonate of protoxide of manganese was diffused, and washing the precipitate, first with dilute nitric acid and then with water. The artificial peroxide thus prepared resisted solutions of chloride of sodium and of caustic potash, even when heated with these liquids in closed tubes to a temperature of 180° by means of a wax bath.

But, notwithstanding the stability of this black oxide of manganese, it is not impossible to obtain from it manganic acid under circumstances which seem to preclude the possibility of any oxidation of the substance during the process by which the manganic acid is exhibited. Mitscherlich † observed and reported the formation of the green manganate of

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* Ann. de Ch. et de Phys., [3.] XII. 381.

† Abhandlungen der Akademie der Wiss. zu Berlin, 1831, p. 218. Ann. de Ch. et de Phys., [2.] XLIX. 114. Pogg. Ann., XXV. 287.

potash, when caustic potash is fused in a retort with peroxide of manganese *without access of air*. Upon such authority this statement must have great weight, although the omission of the details of the experiments renders it impossible to form any opinion of the sufficiency of the evidence upon which it rests. Fortunately the results of Mitscherlich find full confirmation in the recent experiments of Bekétoff.* This observer has shown that, when a mixture of caustic potash and black oxide of manganese is heated, in a closed tube filled with oxygen, to a temperature of 180°, an abundance of the green manganate of potash is formed *without the slightest absorption of oxygen*. Unless these experimental results can be disproved, it seems impossible to escape the conclusion that the substance called peroxide of manganese contains manganic acid, since it yields manganic acid while the ratio of its manganese to its oxygen remains unchanged.

In 1817 Chevillot and Edwards† published an account of some experiments in which they endeavored to prove that the presence of air or oxygen was absolutely necessary to the formation of chameleon from caustic potash and black oxide of manganese. To demonstrate this, they first heated the mixture of these two substances in a silver crucible, within a glass vessel which was filled with nitrogen, and found that no manganate of potash was produced. The amount of heat applied is not stated, but the nature of the apparatus indicates that a high temperature was used. Secondly, they heated the same mixture of caustic potash and black oxide of manganese in an atmosphere of oxygen, and measured the considerable quantity of oxygen absorbed during the formation of the manganate. These experiments seem at first sight absolutely to contradict those of Mitscherlich and Bekétoff; but it is easy to show that they have no such tendency, and that the conclusions which Chevillot and Edwards drew from them were entirely erroneous, though the experiments themselves were perfectly correct and faithfully reported. It is obvious that an absorption of oxygen is just as necessary in order to convert the substance, whose formula would be written $Mn_2O_3\ MnO_3$, *completely* into manganic acid, as it is for the entire conversion of the so-called oxide MnO_2 into the same acid. The same amount of oxygen must be absorbed in changing one gramme of the black oxide of manganese into manganic acid, however the rational formula of that substance may be written. To prove that oxygen is absorbed during the formation of manganate of potash from caustic potash and black oxide of manganese, is therefore not at all to the purpose; the only question is, Can *any* manganate be formed *without* absorption of oxygen? This question the experiments of Mitscherlich and Bekétoff answer in the affirmative. But if manganate of potash is formed from caustic potash and black oxide of manganese without any addition of oxygen, how is the fact of its non-formation in an atmosphere of nitrogen, as proved by Chevillot and Edwards, to be accounted for. We have repeated the experiments of Chevillot and Edwards with a somewhat different apparatus. A combustion-tube of small diameter was nearly filled with copper turnings, and beyond the copper a platinum boat containing a mixture of caustic potash and peroxide of manganese was inserted. The tube was then connected with an aspirator, and a slow current of air was drawn through the hot copper. When time enough had elapsed to secure the complete filling of the tube with nitrogen, the platinum boat was heated gradually up to dull redness without producing a trace of the green manganate. When the tube had cooled, the contents of the boat was a fused, brownish mass. Another experiment, however, showed conclusively that the non-appearance of the green manganate is accounted for by the fact that this manganate cannot exist in an atmosphere of nitrogen at such a temperature. We prepared some manganate of potash in a platinum boat by fusing a mixture of carbonate of potash and black oxide of manganese in the air, and then heated this boat with its contents in an atmosphere of nitrogen by means of the apparatus just described. At a temperature very much below a red heat every trace of the green manganate disappeared, and when the tube was cool the appearance of the contents of the boat was that of a fused, brownish mass, precisely like that described above in the former experiment. Repetitions of the experiments fully confirmed these results, which perhaps ought to have been anticipated, since it seems more than probable that nitrogen would be oxidized in contact with a hot manganate. Similar experiments with an atmosphere of carbonic acid led to the same negative results. It must be borne in mind that our present purpose is merely to show the fallacy of the inferences which Chevillot and Edwards drew from their experiments, which were made at an uncertain but high temperature. We by no means wish to assert that it is impossible to obtain the green manganate of potash from a mixture of caustic potash and black oxide of manganese in an atmosphere of nitrogen, if the temperature be sufficiently low. On the contrary, we have made several experiments which tend to the conclusion that this is perfectly possible under certain conditions. A mixture of caustic potash and natural black oxide of manganese was placed in a glass tube, which was then filled with nitrogen and sealed. Thus hermetically closed, the tube was heated in a wax-bath to 180° for three hours; at the end of the experiment, we found that portions of the mass in the tube had been changed into green manganate of potash, though the greater part seemed to be unaltered. Again, a mixture of potash and the black oxide, artificially prepared, was gently heated in a combustion-tube in a current of nitrogen to a temperature barely high enough to fuse the mass, and the manganate of potash was formed, small in amount, but perfectly unmistakable. In repeating this last experiment, however, we failed quite as often as we succeeded, for it is difficult to heat the mixture hot enough to insure the formation of the manganate without also heating it hot enough to destroy it. Moreover, no experiments, intended to exhibit the formation of manganate of potash in nitrogen from potash and the black oxide, can be conclusive, so long as the experimenter is unable to answer any one who may please to allege that the nitrogen used contained a trace of oxygen. Unless some method of preparing the nitrogen is used which will enable the chemist to assert that the gas is free from oxygen and from all other impurities which might affect the reaction, such experiments will establish nothing. The only conclusive method of testing the question whether manganate of potash can be formed from the black oxide and potash alone, is that so well applied by Bekétoff, who proved that the manganate can be produced from these materials in an atmosphere of oxygen at a low temperature without the slightest absorption of that gas. His experiments were obviously performed with such care that we have thought it superfluous to repeat them.

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* Bulletin de Soc. Chim. de Paris, Séance 13 Mai, 1859, I. 43.

† Ann. de Ch. et de Phys., [2.] IV. 290.

We have been at such pains to review and explain the experiments of Chevillot and Edwards, in order to put the decomposition of the substance called peroxide of manganese into manganic oxide and manganic acid in its true light, as an uncontradicted fact, resting upon the highest authority. If we add to this decomposition of the black oxide of manganese by potash the other fact, that it is a perfectly neutral or indifferent body, possessing none of the properties either of an acid or of a base, we have evidence, not sufficient perhaps absolutely to prove that its true rational formula is $Mn_2O_3\ MnO_3$, but quite enough to show that the formula MnO_2 is no argument for the formula CrO_2, in the face of the demonstration of the true character of the chromate of chromium heretofore given. On the contrary, the fact that the supposed brown oxide of chromium is in reality composed of chromic oxide and chromic acid, gives additional weight to the experimental evidence already accumulated, that the peroxide of manganese is a compound of manganic oxide and manganic acid. There is a striking similarity between the methods of preparing chromate of chromium and manganate of manganese, the more noticeable in view of the very different stabilities and solubilities of the oxides of these two metals. Thus the action of chlorine on chromic oxide gives rise to the formation of chromate of chromium, while its action on the carbonate of manganous oxide produces the manganate of manganese.* Again, the gentle ignition of the nitrate of manganous oxide produces a mixture of manganous oxide with the higher oxides of manganese; this mixture contains so much manganate of manganese that the process has been patented as a method of obtaining a manganese oxide adapted to the preparation of chlorine.† This result corresponds precisely with the result of igniting the nitrate of chromic oxide. Again, the absorption of oxygen by heated chromic oxide exposed to the air, observed by Krüger, finds its exact parallel in the absorption of oxygen by manganous oxide under the same circumstances. A mixture of the higher oxides of manganese is so obtained, and this process of ignition has been long known in the arts as a means of "revivifying" black oxide of manganese, rendering it available for the preparation of chlorine a second time, or through an indefinite series of alternate reductions and oxidations.‡

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* Gmelin's Handbook of Chemistry, IV. 207, Cavendish Soc. Ed.

† Berthier, Ann. de Chim. et de Phys., [2.] XX. 187. Gatty, Eng. Patent Specifications, 22 Aug. 1857, No. 2230, p. 3.

‡ Pfaff. Schweigger's Jour. für Ch. u. Phys., LIII. 122, (1828).
Binks, C. Eng. Patent Specifications, 8 Feb. 1839, No. 7963, pp. 4, 8, and 9.
Ebelmen. Ann. des Mines, [3.] XVII. 517 (1840).
Walters, G. S. Eng. Patent Specifications, 24 Mar. 1843, No. 9676.
Balmain, W. H. " " " 31 Mar. 1855, No. 723, p. 4.
Dunlop. " " " 22 Nov. 1855, No. 2637, p. 3.
Barrow. " " " 26 Feb. 1856, No. 485, pp. 4, 9.
Elliot. " " " 13 Oct. 1856, No. 2392, p. 4.
Pattinson. " " " 21 Oct. 1856, No. 2475.
Gossage. " " " 8 Nov. 1856, No. 2630, p. 7.
Reissig. Ann. der Ch. u. Pharm., CIII. 27 (1857).
In several of these specifications the removal of alumina and sesquioxide of iron

While it is much easier to obtain the manganate of manganese in a state of tolerable purity than it is to prepare the chromate of chromium, because of the greater insolubility of the first substance, it would nevertheless be very difficult, to say the least, to precipitate it by the method of double decomposition. We can readily mix chromate of potash and a normal salt of chromic oxide, and throw down the chromate of chromic oxide: till we can prepare a pure and neutral manganate of potash, the true composition of the manganate of manganic oxide cannot be illustrated in this way.

IV. Other Chromates of Chromic Oxide.

Under the head of "Bichromate of Chromic Oxide" the English Editor of Gmelin's Handbook of Chemistry* has described two processes, neither of which has any connection with the name and formula at the head of the paragraph; the first is the description of a washed, and therefore basic, chromate of chromic oxide, prepared by Traube,† identical with the substance analyzed by Rammelsberg, as Traube himself remarks, and having the same formula by Traube's analysis, viz. $(Cr_2O_3)_3\ (CrO_3)_2$; the second is the description of the mode of precipitating the chromate of chromic oxide, $Cr_2O_3\ CrO_3$, from chrome alum by chromate of potash in the manner we have fully explained.

For the existence of what the translator of Gmelin's ‡ Handbook calls the "Neutral Chromate of Chromic Oxide," with the formula $Cr_2O_3\ 3\ CrO_3$, there seems to be no sufficient evidence. Unverdorben, Berzelius, and Maus have proved beyond a question, what hardly required proof, that when heated above the melting point chromic acid is ultimately resolved into oxygen and chromic oxide. Traube § has thought to show that by using a temperature but little above 250° a definite chromate can be obtained, corresponding to the formula $Cr_2O_3\ 3\ CrO_3$. By heating a quantity of chromic acid to this re-

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is described, preparatory to the roasting of the manganous salt or oxide. The more manganic acid formed by the roasting the better, — may not then the admixture of a certain amount of these bases be chemically advantageous? Very possibly there are mechanical advantages to be gained by their removal.

* Handbook of Chemistry, IV. 115 (Cavendish Soc. Ed.).

† Ann. der Ch. u. Pharm., LXVI. 108 (1848).

‡ Handbook of Chemistry, IV. 116 (Cavendish Soc. Ed.).

§ Ann. der Ch. u. Pharm., LXVI. 106 (1848).

quired temperature he obtained a black mass which had taken the shape of the crucible; this he powdered and digested with water, with the expectation of dissolving that portion of the chromic acid which had not been affected by the heat; the wash-water after some days still remaining yellow, he concluded that the substance itself gradually dissolved, and proved this to his own satisfaction by analyzing two portions, one of which had been washed more than the other, with the same result, viz. 57.93 per cent of chromium and 42.07 of oxygen. These figures correspond to the formula Cr_2O_3 3 CrO_3. Now chromic acid contains 52.23 per cent of chromium and chromic oxide 68.62 per cent, and in changing from the first into the second, under the influence of a moderate heat, the heated substance will at some moment contain 57.93 per cent of chromium; before that moment it would contain less, after that moment more. We were not so fortunate as to hit on the right time for stopping the experiment. We subjected a mass of chromic acid to a temperature a little above 250° for three hours, and obtained a brownish black substance, such as Traube has described, which, powdered and boiled with water, imparted a faint yellow color to the liquid. Analysis showed that it contained 54.12 per cent of chromium. It is quite clear that any substance prepared in such a way must be a mixture, and that the particular mixture analyzed by Traube has no claim to the name and formula of a definite compound.

Still another hypothetical chromate, called " Soluble Brown Chromic Oxide or Acid Chromate of Chromic Oxide," figures in Gmelin's Handbook (*loc. cit.*). Maus and many others have made a solution of hydrated chromic oxide in aqueous chromic acid, but Maus alone has analyzed the solution; we have already expressed our opinion that the liquid he analyzed was only an indeterminate mixture (p. 211). The observation and the conjecture of Berzelius, cited by Gmelin in this paragraph, we have already remarked upon; the precipitate which Berzelius speaks of is the chromate of the formula Cr_2O_3 CrO_3.

To sum up the case, — there is not a particle of evidence of the existence of any chromate of chromium containing more than one equivalent of chromic acid. Such may be hereafter discovered, but it does not seem probable that they will be found to be insoluble compounds. Until the realities are made known to us, why cumber the science with names and formulæ, which fill no gaps, extend no analogies, bridge no difficulties, but are merely a perplexity and a hinderance? It has been too much the custom to call the chromate of the formula Cr_2O_3 CrO_3

the *basic* chromate of chromium; this proceeds on the assumption that there is some other salt better entitled to the name of normal or neutral chromate, as, for example, the imaginary chromate containing three equivalents of chromic acid. Until some such chromate is discovered, the word *basic* would be better omitted from the name of the only definitely determined chromate of chromium.

Professor G. P. Bond exhibited a drawing of the great nebula surrounding the star θ Orionis representing its appearance in the twenty-three-foot refractor of the Observatory of Harvard College.

The feature to which attention was particularly directed was the spiral structure of the principal masses of light, or, more correctly, the tendency to an arrangement in elongated wisps or whirls, sweeping outward from the bright region of the Trapezium. A disposition of the nebulosity in some localities to radiate from the vicinity of the Trapezium, noticed in the memoir published by Professor W. C. Bond in 1848, has repeatedly attracted attention in subsequent years. The idea of a spiral character in the radiations had even been suggested, without however presenting itself definitely to the mind as the true conception of the leading features of the nebula.

During the past winter, opportunities were taken to review the whole region, with particular reference to this peculiarity; attention being given exclusively to the arrangement of the diverging wisps of nebulosity, and the alternating dark spaces by which they are separated from each other. A particular scrutiny of the latter was of considerable assistance in tracing the fainter convolutions. The form and disposition of the whirls were thus defined by two independent processes, the nebula being first sketched as a bright object on a dark ground, and, again, its darker openings and channels as dark objects on a white ground.

The quarter designated in Herschel's chart * as the *Regio Godiniana* was first explored. The nebulosity was here resolved into an assemblage of three or four long wisps, interlaced with each other, or crossed by offsets; these were ultimately traced from a point near the northern margin of the *Sinus Magnus*, over the whole length of the *Regio Picardiana* and the *Regio Godiniana*, forming a sweep of 120°. After passing the well-defined northern boundary of the last-named region, and beyond Herschel's stars *o* and *ξ*, these wreaths bend rather suddenly, and tend towards the south-preceding direction. Indications of their presence in this quarter are imperfectly suggested in Lassell's and in Sir J. Herschel's latest drawing. From this point feeble traces exist for 10′ or 15′ in a south-preceding direction. Their course over the *R. Picardiana* gives a decidedly reticulated aspect to the whole region; but, though bright, they are here so closely intertwined and connected by offsets, that it is a matter of no little difficulty to gain a clear comprehension of their proper relations. The complexity of the details is further increased by several offshoots from this quarter, which cross over into the adjacent *R. Derhamiana;* still the general effect is easily recognized.

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* Mem. Astr. Soc., Vol. II.

From the southern corner of the *Regio Picardiana*, and from those parts of *R. Derhamiana* and *R. Huygeniana* which lie near the Trapezium on its north-preceding and preceding sides, a number of narrow and bright branches diverge, their extremities tending also to the south-preceding direction. Some of these cross the *R. Gentiliana* and seem to merge together, forming a nebulous mass, which can be followed through an arc of 10′ or 15′. Others, which are less curved, originate near the *Sinus Gentilii;* these are narrow and somewhat tortuous.

It is to be noticed that the initial direction of the wreaths (*Nebelstreifen*) changes continuously from an angle of position of 330° on the northern margin of the *Sinus Magnus*, to one of 220°, or less, at the *S. Gentilii*, and the sweep of the curve correspondingly diminishes, so that throughout the whole nebulous region preceding the sharply defined apex of the *R. Huygeniana*, the extremities of the filaments have a pretty uniform tendency in the angle of position 220°. As soon, however, as we pass to the fields on the following side of the apex, a change is immediately apparent. The ultimate direction being about in the angle 160°. The principal group of wisps results from the resolution of the *R. Messeriana*, and the region between the Trapezium and the *Proboscis Minor*, including both these features, into four or five distinct wreaths having a common initial direction in the angle of position 110°. The very bright nebulosity lying between the *S. Gentilii*, the Trapezium, and the *R. Subnebulosa*, cannot be resolved into a regular structure, but three or four condensed spots, constituting the most brilliant part of the nebula close on the south-preceding side of the Trapezium, are plainly distinguished as tufts or curled offsets from a prominent wisp of light which extends from its origin, near the Trapezium, across the *R. Gentiliana.*

The general aspect of the greater part of the nebula is therefore that of an assemblage of curved wisps of luminous matter, which, branching outward from a common origin in the bright masses in the vicinity of the Trapezium, sweep towards a southerly direction, on either side of an axis passing through the apex of the *Regio Huygeniana*, nearly in the angle of position 180°. About twenty of these convolutions have been distinctly traced, while others giving a like impression are too faint or too intricate to be subjected to precise description. It may therefore be properly classed among "the spiral nebulæ," under the definition given by their first discoverer, Lord Rosse; including in the term all objects in which a curvilinear arrangement, not consisting of regular re-entering curves, may be detected.

That the existence of this feature in the great nebula of Orion should have hitherto escaped notice, after the many careful scrutinies to which it has been subjected, with the help of the largest instruments and the most skilful observers, may seem scarcely credible; a few words of explanation on this point will not therefore be amiss. It is to be ascribed partly to the confusing effect produced by the crossing and intersection of the principal *striæ* and of their offsets, which the eye cannot unravel without the aid of some clew to their mutual relation and significance; and partly also to the faintness of some of the details, which are, nevertheless, very essential features in a correct apprehension of its structure, supplying, as they do, what would otherwise appear as breaks of continuity, and assisting materially in the recognition of a principle of regularity pervading the whole structure. Until the law of relation and continuity in the several parts of such an object is entertained in the mind, it must remain an incoherent, confused assemblage of material, having no orderly or connected arrangement.

The change from the previous notion of its configuration is not more considerable than that which took place with reference to the celebrated nebula 51 Messier, in which the original discovery of the spiral arrangement was made. This object had been subjected to a careful examination and description by both the Herschels, but neither their drawings nor descriptions furnished the slightest intimation of a spiral structure. It deserves particular notice, too, that there was no want of sufficient optical power to exhibit the appearance in question; for the spirality of 51 Messier is seen with perfect distinctness in a refractor of 15 inches' aperture, and must certainly be within reach of the twenty-foot Herschelian reflectors. Nor can it for a moment be thought that the earlier observations and delineations were in any proper sense erroneous. They were simply made at a great disadvantage, in the absence of a clear conception of the general plan of structure presented in the object. Some of the details indispensable to its recognition, being only faintly presented, were overlooked, or, appearing by mere suggestions and glimpses of vision, they conveyed an erroneous impression; in this way the mutual relation of the various parts came to be entirely misconceived. The missing links were supplied by the larger optical power of Lord Rosse's telescope, too plainly not to insure notice; and the nebula then presented itself under a totally different aspect. Instances of similar revelations, completely at variance with previous conjectures, have indeed so often occurred in the history of astronomical discovery, that the process ought to be regarded as the ordinary rule, rather than as an unusual exception.

Professor Bowen read a paper arguing against the wisdom of legal enactments requiring banks to keep a fixed and constant proportion of specie in reserve.

Mr. Felton read a paper on the honey of Mount Hymettus, of which he had received a supply from the Rev. Dr. Hill of Athens. He gave an account of the Grecian bee, citing passages from the poets, beginning with Homer: next, the various occasions, religious and social, on which honey was used by the ancients were enumerated. The employment of honey in the medical practice of the Athenian physicians, especially by Hippocrates and Galen, was explained, and passages were cited from the writings of Hippocrates. The next topic was a philological one, the use of honey as a term of comparison, and the frequency with which the word μέλι (honey) is compounded with other words in descriptive epithets. This was shown by a series of passages in the poets and prose-writers, from Homer to Plato and Aristotle. The reputation of the honey of Mt. Hymettus in ancient times was then illustrated by quotations from Strabo and Pliny; and in modern times, by the testimony of the old traveller, Wheeler, and others. The wild thyme which flourishes in abundance on the mountain, and which gives its peculiar flavor and fragrance to the honey, was described, and specimens exhibited.

Greece has been overrun, it was remarked, by hostile and barbarous hordes. Persians, Gauls, Romans, Vandals, Goths, Slavonians, Albanians, and Turks have successively swept over the land, until some, like Fallmereyer, have come to the conclusion that the ancient Hellenic population have been utterly displaced, and not a drop of Hellenic blood flows in Grecian veins. This is a paradox, as any one may see who will visit Dr. Hill's school or the Panepistemion of Otho, or the Parthenagogeion, and look into the animated countenances which might furnish models for another Panathenaic procession. But let the speculative sceptic doubt this if he pleases; even he cannot doubt that the bees of Hymettus are descended in a bee-line from those that clustered round the lips of the infant Plato as he slept among the myrtles while his parents were sacrificing to the Hymettian nymphs.

> "And still his honeyed wealth Hymettus yields;
> There the blithe bee his fragrant fortress builds,
> The free-born wanderer of thy mountain air."

A small quantity of the Hymettus honey was placed on the table as a further and final illustration of the subject.

Four hundred and ninety-fourth meeting.

April 11, 1861. — MONTHLY MEETING.

The PRESIDENT in the chair.

Mr. Charles G. Loring announced the death, upon the same day, of two venerable and distinguished Fellows of the Academy, viz. Chief Justice Shaw and Judge White, in the following terms: —

Mr. President: Since the last meeting of the Academy, and within the lapse indeed of a few days, two of its most venerated members, whose age, social position, and eminent endowments added much to its dignity and influence, having been called from earth by the angel of death, it becomes us to turn from our ordinary avocations for a moment in contemplation of their departure, and to place upon record a testimonial of our appreciation of their worth. And as both were in the